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HIGH-STRENGTH CERAMICS BASED ON ZIRCONIUM DIOXIDE POWDER

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The method of coprecipitation of components was used to obtain disperse powders of tetragonal zirconium dioxide stabilized by Y_2O_3 , Yb_2O_3 and a combined additive ($Y_2O_3 + CaO + MgO$). The technological parameters of the processes of synthesis and preparation of initial ZrO_2 powders intended for ceramics with elevated strength parameters are proposed.

The transformation-strengthened products based on ZrO_2 have an increased strength due to a partial polymorphous transformation of a part of the material from the tetragonal phase into the monoclinic phase. Such articles can be produced from submicron powders with a maximum content of the tetragonal phase [1]. The tetragonal modification is stabilized by introducing oxide additives that form solid substitution solutions with ZrO_2 . In transformation strengthening of ceramics, the stability of the tetragonal phase in the initial powder is provided by the minimum possible grain size and by the quantity of the stabilizing additive, which facilitates the tetragonal-monoclinic transformation after sintering of articles [2, 3].

There are many methods for producing disperse powders of ZrO_2 solid solutions. Among them, the method of coprecipitation of components is the simplest and does not require costly or toxic reactants. This method ensures the most homogeneous distribution of the stabilizer oxides in the crystalline lattice of ZrO_2 and the production of the most chemically homogeneous finely dispersed powders, which makes it possible to reduce the energy consumed in firing of articles.

To perform chemical coprecipitation of components, it is necessary to prepare aqueous or acid solutions of zirconium compounds and the stabilizing additive, to mix them in a pre-set ratio, and to precipitate insoluble or hardly soluble compounds (hydroxides, carbonates, oxalates) [4]. The precipitated compounds are separated by filtering, thoroughly washed from the residue of the mother solution, dried, and subjected to heat treatment. The precipitate is heated to a temperature at which a new compound is fully synthesized. For each combination of precipitated elements, it is neces-

sary to select a precipitator, its concentration, pH, and the temperature conditions of drying and heat treatment. Homogeneous powders of high dispersion are obtained as a result of this synthesis.

The present study considers certain specifics of the technology of producing disperse ZrO_2 powders by coprecipitation of hydroxides using ammonia. The stabilizing additives were either individual oxides (Y_2O_3 , Yb_2O_3 , MgO , and CaO) or a combination of additives (Y_2O_3 , MgO , and CaO).

Solid solutions were obtained using zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, calcium carbonate, magnesium carbonate, yttrium and ytterbium oxides, and aqueous solution of ammonia. The precipitated powders were heat-treated at 450 – 1400°C in an electric furnace with a 2-h exposure at the final temperature. The qualitative and quantitative phase analysis of the powders was carried out on a DRON-UM1 x-ray unit with CuK_α radiation. The accuracy in determining phases was $\pm 5\%$. The elemental analysis was carried out using the atom-absorption method on a Perkin-Elmer spectrophotometer. Aggregated powders were milled in a 10-liter ball mill with balls 5 – 10 mm in diameter made of ShKh-15 steel. The specific surface area was determined with a BET method based on thermal desorption of argon on an OÉTs-IK-1 chromatograph. The average grain size of the powders (μm) was estimated from the formula

$$d_{av} = \frac{60,000}{\gamma S_{sp}},$$

where γ is the density, g/cm^3 and S_{sp} is the specific surface area, cm^2/g .

Zirconium oxychloride was dissolved in water at a temperature of around 90°C. The ZrO_2 concentration in the solu-

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TABLE 1

Molar content of stabilizing oxides, %				Specific surface area of powders, m ² /g, after calcination at temperature, °C			Molar content of monoclinic phase, %, after calcination at temperature, °C		
Yb ₂ O ₃	Y ₂ O ₃	CaO	MgO	700	900	1000	700	900	1000
2.0/1.9*	—	—	—	6.0	4.5	3.1	15	10	10
2.5/2.6	—	—	—	6.0	4.3	2.8	10	10	10
3.0/3.1	—	—	—	5.9	4.3	2.9	5	5	5
3.5/3.4	—	—	—	5.7	4.4	3.0	0	0	0
4.0/3.2	—	—	—	5.8	4.2	2.7	0	0	0
4.5/4.7	—	—	—	5.7	4.1	2.7	0	0	0
—	0.1/0.1	—	—	6.1	4.4	3.3	40	60	90
—	0.5/0.7	—	—	6.2	4.1	3.2	20	40	60
—	1.0/0.9	—	—	6.0	4.2	3.1	15	30	50
—	1.5/1.5	—	—	6.0	4.1	3.0	15	20	30
—	2.0/1.9	—	—	5.9	4.0	2.9	10	15	25
—	2.5/2.7	—	—	5.8	4.1	2.8	5	5	15
—	3.0/2.9	—	—	5.8	4.1	2.9	0	0	5
—	3.5/3.6	—	—	6.0	4.1	2.7	0	0	0
—	4.0/4.1	—	—	5.6	4.0	2.7	0	0	0
—	4.5/4.6	—	—	5.8	3.9	2.8	0	0	0
—	—	10.0/8.7	—	19.4	6.9	4.3	30	30	25
—	—	—	10.0/7.6	25.3	14.1	2.9	40	50	70
—	3.0/2.9	2.0/1.8	4.0/3.6	7.1	4.8	3.4	0	0	0
—	2.6/2.5	0.4/0.5	1.0/1.0	6.8	4.7	3.6	0	0	5
—	2.6/2.5	0.5/0.6	0.9/0.8	6.7	4.3	3.4	0	0	10
—	2.3/2.3	0.5/0.4	1.0/0.9	6.8	4.8	3.5	0	5	10
—	2.0/2.0	0.5/0.5	1.0/0.9	6.9	4.6	3.4	10	15	15
—	2.0/2.0	0.5/0.5	1.0/0.9	6.9	4.6	3.4	10	15	15
—	1.6/1.7	1.2/1.1	1.4/1.2	6.8	4.4	3.4	5	10	10
—	1.6/1.7	0.4/0.4	1.0/0.8	6.7	4.5	3.5	20	20	25
—	1.6/1.7	0.4/0.5	2.2/2.0	6.8	4.8	3.6	5	10	10

* Above the line: additive content introduced into the initial solution; below the line: content of additives after calcination

tion was 320 – 350 g/liter. The stabilizer additives were dissolved in boiling hydrochloric acid. The hot solutions of ZrO₂ and stabilizing additives were mixed in preset concentrations and poured into a 10% ammonia solution under constant stirring. The quantity of the ammonia solution was selected in such a way that the mother solution after the end of the precipitation have pH = 9. The precipitate was vacuum-filtered and heat-treated.

An analysis revealed that the concentrations of Y₂O₃ and Yb₂O₃ additives in the filtered precipitate virtually did not change, whereas CaO and MgO additives to a large extent (up to 80%) were removed together with the mother solution. The latter is due to the formation of water-soluble ammonium complexes of the [Mg(NH₃)₆]Cl₂ and [Ca(NH₃)₆]Cl₂ types. To prevent the dissolution of the specified oxides, ammonium carbonate was added to the initial ammonia solution in a quantity 1.5 – 2 times exceeding the quantity required for bonding calcium and magnesium in the respective carbonates, which increased the degree of precipitation of the latter to 80 – 90%. Apparently, what happens in the presence of ammonium carbonates is not separate precipitation of the components (zirconium and yttrium in the form of hydroxides, calcium and magnesium in the form of carbonates) but the formation of a complex zirconium hydroxide-carbonate

compound with yttrium, calcium, and magnesium ions incorporated in its structure. As evidence supporting this hypothesis is the fact that the derivatograms of the precipitated sediments do not exhibit a thermal effect corresponding to the emergence of individual compounds.

Table 1 lists the results of determining the specific surface area and the phase composition of heat-treated ZrO₂ powders with various contents of stabilizing additives. It can be seen that the specific surface area of precipitated powders heat-treated at the same temperature virtually does not depend on the type and the quantity of the additive. The heat-treatment temperature has the most significant effect on the specific surface area of powders.

As the precipitates are heated, their specific surface areas monotonically decrease, except for the powders containing CaO and MgO stabilizing additives in an amount of 10% (here and elsewhere the molar content is indicated, unless otherwise specified). The latter compositions exhibit an anomalous increase in their specific surface area at a temperature of around 700°C (Fig. 1). This maximum observed in the composition containing 10% CaO and MgO is due to the formation of supersaturated solid solutions of CaO and MgO in ZrO₂, which disintegrate at the specified temperature and release free CaO and MgO, which later, under further heat-

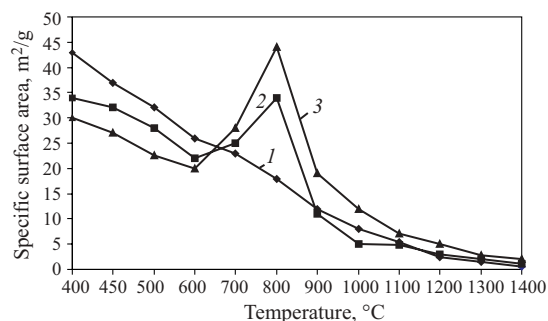


Fig. 1. Variation of the specific surface area of ZrO_2 -based solid solutions depending on the calcination temperature. The molar content of MgO stabilizer (%): 1) 5; 2) 10, 3) 20.

ing, again dissolve in ZrO_2 and form high-temperature equilibrium solid solutions.

The crystallization of solid solutions of ZrO_2 under heating of the coprecipitated components occurred within a temperature interval of 450–500°C. According to the data of x-ray phase analysis, the cubic or tetragonal ZrO_2 (it was impossible to identify these phases separately due to the blurred diffraction maximums) is formed in the considered compositions at these temperatures, regardless of the additive content. The specific surface area of the coprecipitated powders is 30–50 m^2/g , which correlates with an average particle size of 0.02–0.03 μm .

After heat treatment at 700–1100°C, the monoclinic phase of ZrO_2 was registered in some powders. The formation of up to 90% monoclinic phase in firing was observed in the powders with a low content of the stabilizing additive (0.1–2.0% Y_2O_3). The content of the monoclinic phase in these compositions increases with increasing firing temperature and also with a decreasing concentration of the stabilizer. When the content of Y_2O_3 and Yb_2O_3 stabilizers is over 3%, the monoclinic phase is not registered in the powders. It is known that the stability of the tetragonal phase to a large extent is determined by the particle size [5]. The calculations established that the mean size of the crystallites under heat-treatment temperatures of 700, 900, and 1000°C is 0.15 ± 0.05 , 0.25 ± 0.05 , and 0.30 ± 0.10 μm , respectively. Apparently, despite the small mean size of the crystallites in this case, a certain number of crystallites is formed in calcination, whose size exceeds a critical size and which in cooling are transformed into monoclinic ones.

It should be noted that for the 2.0–4.5% content of Y_2O_3 and Yb_2O_3 additives, the properties of powders and their behavior under heat treatment are identical. On introducing a combined additive ($\text{Y}_2\text{O}_3 + \text{CaO} + \text{MgO}$), the specific surface area of the powders is larger and the total content of additives required to stabilize the tetragonal phase of ZrO_2 has to be higher than in the case of Y_2O_3 or Yb_2O_3 additives.

Under constant conditions of the synthesis of powders (the concentration of the ZrOCl_2 solution, the heat-treatment

conditions), no substantial distinctions in sizes of the crystallites of the solid-solution powders were registered.

Thus, the method of coprecipitation of components makes it possible to obtain size-reproducible submicron powders based on ZrO_2 with small quantities of stabilizing additives. The optimum content of the stabilizing additive is 3.0–3.5% Y_2O_3 , and the heat treatment of coprecipitated powders at 1000–1100°C guarantees the production of the tetragonal ZrO_2 phase. The specific surface area of the powders heat-treated at 1000–1100°C is somewhat smaller than in the powders heat-treated at lower temperatures (this choice is determined by the most complete incorporation of yttrium oxide in the ZrO_2 lattice).

With a high specific surface area of the solid solution powders and a low size of the crystallites, the powders after heat treatment aggregate in particles of size 20–200 μm . The aggregated powders are inert and in firing do not sinter into a pore-free material up to temperatures of 1900–2100°C. To crush the aggregates to the initial crystallite size (about 0.1 μm), mechanochemical activation of powders was carried out for the purpose of lowering the sintering temperature.

The powder of ZrO_2 solid solution containing 3.5% Y_2O_3 calcined at 1100°C was subjected to milling. The effect of the material : balls : water ratio and the milling duration on the disaggregation of the powder and the concentration of milled iron was investigated. The degree of disaggregation of the powder was estimated based on the content of grains sized greater than 1 μm (determined with an optical microscope). The experimental results are listed in Table 2.

It can be seen that the degree of disaggregation of powders increases as the milling duration increases, regardless of the material : balls : water ratio; however the concentration of milled iron in this case grows as well. As the material : water (M : W) ratio increases, the effectiveness of milling drops, and at $M : W > 1$, the required degree of disaggregation is not reached even after 110 h of milling (Table 2, experiment 13). Although at low values of $M : W$ (≤ 0.5) the disaggregation of the powder occurs soon enough, the general efficiency of the mill operation in such conditions is low, as the yield of the milled product is not high and constitutes $\leq 10\%$ of the total mill charge (about 30 kg of ZrO_2 powder). At $M : W \geq 1$, the milled suspensions have a high viscosity, and the milling stops.

To decrease the viscosity of the milled suspension, we tried introducing Ca(OH)_2 , NaOH , and Na_2CO_3 electrolytes, which raise the pH to 10–11. The most effective was the Ca(OH)_2 additive in an amount of about 0.1% of the weight of the charged material. This additive not only accelerated the disaggregation by 15–20% but also decreased the iron milled from 4.0–5.0 to 2.5–3.0%, presumably due to a weakened interaction between the milling bodies and water in an alkaline medium.

The optimum conditions selected for milling aggregated ZrO_2 powder in a 10-liter mill prescribe a material : balls : water ratio equal to 4 : 8 : 6, a milling duration of 50 h, and a

TABLE 2

Experiment	Mill charge, kg				Mass content of particle sized > 1 μm , % after milling during, h					
	material	balls	water	M : W	10	30	50	70	90	110
1	1	12	6	0.17	< 1/2.1*	< 1/3.5	< 1/4.0	—	—	—
2	2	8	6	0.33	5/1.8	1/2.5	< 1/3.6	< 1/4.7	< 1/5.1	< 1/5.2
3	2	12	6	0.33	5/2.0	< 1/3.0	< 1/4.2	—	—	—
4	3	6	6	0.50	30/1.0	15/2.0	5/3.0	< 1/3.6	< 1/4.1	< 1/4.5
5	2	8	4	0.50	30/1.2	10/3.0	< 1/4.0	< 1/4.5	< 1/5.0	< 1/5.1
6	3	10	6	0.50	5/2.0	< 1/3.0	< 1/4.0	1/4.9	< 1/5.1	< 1/0
7	3	12	6	0.50	5/2.1	< 1/3.1	1/4.0	< 1/5.0	< 1/5.5	< 1/0
8	4	6	6	0.67	40/1.1	25/2.0	10/2.8	5/4.0	< 1/4.5	< 1/5.1
9	4	8	6	0.67	30/2.0	15/2.2	5/3.0	< 1/4.0	< 1/4.8	< 1/5.0
10	4	8	4	1.00	40/1.5	30/2.0	20/3.0	10/3.8	5/4.5	5/5.0
11	5	10	5	1.00	50/0.8	35/0.9	20/1.0	10/1.5	5/2.0	5/3.0
12	4	12	4	1.00	20/2.0	5/3.0	< 1/3.8	< 1/0	< 1/0	< 1/0
13	6	8	4	1.50	80/1.0	50/1.5	30/2.2	25/2.5	25/3.0	25/3.5

* Above the line: content of particles of size < 1 μm in milled powder; below the line: mass content of milled iron.

content of $\text{Ca}(\text{OH})_2$ electrolyte equal to 0.1% of the weight of the material. These conditions ensure a minimum quantity of iron milled, a maximum degree of grinding of the powder, and a maximum efficiency of the mill.

After grinding in a ball mill under the optimum conditions, the weight content of the milled iron in the powder amounts to 3.05%. The presence of iron oxides in the initial powders facilitates the formation of the cubic and the monoclinic phases in firing of ZrO_2 -based articles and impairs their properties [6]. To remove iron oxides, various acids were added to the milled suspension in an amount of 1 mole per 10 moles ZrO_2 (variant 1) and 3 moles per 10 moles ZrO_2 (variant 2). The suspension was mixed with an acid and held for 2 days. After the sediment settled, the liquid phase was decanted, distilled water was poured over the sediment, which was stirred and held for 2–3 days, and then the liquid was decanted. Such decanting was repeated until the pH of the suspension became equal to 2–3. The sediment, the solution, and the washing-off liquid were analyzed for the content of ZrO_2 , Y_2O_3 , and Fe_2O_3 . It follows from the data presented in Table 3 that:

— acid treatment, except for oxalic acid, results in a substantial removal of iron from the suspension; the most effective are hydrochloric, perchloric, and acetic acids; oxalic acid is not effective in removing milled iron;

— a loss of zirconium and yttrium oxides occurs in acid treatment; the removal of Y_2O_3 from the solid solution is significantly more intense and proceeds mainly from the surface layer of the powder particles to a depth of 0.3–0.7 nm;

— an increase in the concentration of acid facilitates a more effective removal of iron from the suspension, as well as an increased removal of zirconium and yttrium oxides.

All acids considered (except for oxalic acid) may be recommended for a complete removal of milled Fe_2O_3 . However, the densest sediments (cakes) of milled and washed-off powder were formed only in using hydrochloric, perchloric, and acetic acids. In other cases, the sediment was loose and

TABLE 3

Acid	Variant	Weight loss, %			Mass content, %, in solid phase after washing off		
		ZrO_2	Y_2O_3	Fe_2O_3	ZrO_2	Y_2O_3	Fe_2O_3
HCl	1	1.1	10.6	84.5	94.1	5.7	0.45
	2	2.1	14.3	97.4	94.3	5.3	0.08
HNO_3	1	0.6	6.0	74.2	93.7	6.0	0.96
	2	1.4	13.1	93.2	94.3	5.4	0.21
HClO_4	1	0.5	6.9	76.5	93.9	5.9	0.80
	2	1.0	13.0	96.8	94.3	5.5	0.10
CH_3COOH	1	0.1	3.2	85.8	93.4	5.8	0.09
	2	0.3	7.4	98.8	94.0	5.2	0.10
$\text{H}_2\text{C}_2\text{O}_4$	1	0.9	4.5	1.4	90.7	6.2	3.01
	2	1.7	2.6	3.2	90.4	6.4	2.86

little suitable for molding articles. With $\text{pH} = 2 - 3$, the liquid above the sediment treated with hydrochloric, perchloric, and acetic acids remained opaque even after 1 month of sedimentation. The concentration of ZrO_2 in these liquids did not vary after 7 days of sedimentation and amounted to 0.2–0.3 g/liter. Apparently, a hydrolysis of the diluted zirconate solutions takes place in this case with the formation of a stable sol.

The experiments substantiated the expedience of using hydrochloric acid for washing milled iron of ZrO_2 (as acetic and perchloric acids are more expensive and more dangerous to handle).

Considering that complete washing off of iron oxide at room temperature requires a long time and consumes substantial quantities of hydrochloric acid, we analyzed the effect of heating and adding oxidizers (nitric acid and hydrogen peroxide) in using hydrochloric acid in an amount of 1 mole per 10 moles of ZrO_2 (Table 4). It can be seen that heating and adding oxidizers increase the degree of removal of iron oxide, the effect of the oxidizers being more significant. The addition of hydrogen peroxide increases the loss of

TABLE 4

Additional treatment	Weight loss, %			Mass content, %, in solid phase after washing off		
	ZrO ₂	Y ₂ O ₃	Fe ₂ O ₃	ZrO ₂	Y ₂ O ₃	Fe ₂ O ₃
Heating up to 90°C for, h:						
0.5	1.4	11.0	90.5	94.1	5.7	0.22
2.0	1.6	11.6	92.3	94.0	5.7	0.21
4.0	1.7	11.9	93.6	94.2	5.6	0.21
8.0	1.7	12.0	93.9	94.3	5.6	0.19
Introducing hydrogen peroxide, mole, per 10 moles of ZrO ₂ :						
0.05	1.6	11.3	93.5	94.0	5.7	0.21
0.10	1.8	11.8	94.8	94.3	5.6	0.17
0.15	1.7	12.7	96.9	94.3	5.5	0.11
0.20	2.0	13.5	97.4	94.2	5.6	0.09
0.25	2.0	14.0	98.0	94.4	5.5	0.09
Introducing nitric acid, mole, per 10 moles of ZrO ₂ :						
0.05	1.5	10.3	96.2	93.9	5.8	0.13
0.10	1.6	9.8	98.1	94.0	5.9	0.08
0.15	1.6	8.3	98.2	93.6	6.0	0.08
0.20	1.8	10.6	98.5	93.7	5.8	0.07
0.25	1.7	11.5	99.1	93.9	5.7	0.07

yttrium oxide, and the introduction of nitric acid, on the contrary, perceptibly decreases the removal of yttrium oxide from the material. It has been established that the introduction of 0.15 mole of HNO₃ per 10 moles of ZrO₂ decreases the loss of Y₂O₃ by 2.3%. After washing the powder using nitric acid, the mass content of Fe₂O₃ amounts to 0.07 – 0.09%, which is comparable to the content of Fe₂O₃ in the initial material before its grinding in the ball mill (0.08%). It should be noted that after acid treatment, the mass contents of SiO₂ and Al₂O₃ impurities in the powder did not vary (the initial material contained 0.15% SiO₂ and 0.04% Al₂O₃).

Thus, the following process parameters may be recommended for producing disperse ZrO₂ powders with a maxi-

mum content of the tetragonal phase using the method of ammonium coprecipitation of hydroxides:

- a minimum content of the additives allowing for the stabilization of ZrO₂ in the tetragonal modification: 3.0 – 3.5% Y₂O₃ or Yb₂O₃;
- concentration of ZrOCl₂ solution equal to 350 g/liter converted to ZrO₂;
- heat treatment of coprecipitated powders at 1000 – 1100°C with exposure at this temperature for 2 h;
- grinding of aggregated powders in a ball mill in the presence of Ca(OH)₂ electrolyte in the amount of 0.1% of the weight of the material for 50 h, the material : balls : water ratio being equal to 4 : 8 : 6;
- washing milled iron off powders using hydrochloric acid (of concentration 1 mole HCl per 10 moles ZrO₂ or 2.9% of the weight of the ZrO₂ powder) in the presence of nitric acid as an oxidizer (of concentration 0.15 mole HNO₃ per 10 moles ZrO₂ or 0.8% of the weight of the ZrO₂ powder).

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